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The Chemical Composition of Lakes in the

North-central United States

bу

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CONTENTS

Abstract	1
Introduction	3
Description of the region	4
Geology	4
Groundwaters	6
Climate	7
Vegetation	7
Sources of data	8
Chemical classification of surface lake waters	9
Concentrations and ionic proportions	19
Total cations and anions	19
Trends in ionic concentration	33
Trends in ionic composition	36
Q-mode factor analysis	42
Temporal variability in concentration and composition	44
Unusual situations	45
Color	49
Discussion	51
References cited	55
APPENDTY	60

TABLES

Table I	. 1	the volume-weighted mean ionic composition of atmospheric	
	p	precipitation in northeastern Minnesota, compared with the	
	c	composition of the four most dilute group I lakes (in	
	V	Visconsin)	17
		ILLUSTRATIONS	
Figure	1.	Map of bedrock geology of the north-central United States.	5
Figure			
		logarithmic intervals for all 1,133 lakes in the north-	
		central United States	10
Figure	3,	Frequency distributions, (by state) of specific	
		conductivity at logarithmic intervals for 1,133 lakes in	
		Wisconsin, Minnesota, and the Dakotas	11
Figure	4.	The geographical distribution (by county) of lakes in the	
		north-central United States, grouped (I to V) in order of	
		increasing specific conductivity	12
Figure	5.	Belt transects of specific conductivity in lakewaters of	
		western Minnesota	13
Figure	6.	The \log_{10} relationship between total cations and	
		specific conductivity	14
Figure	7.	The relationship between pH and \log_{10} specific	
		conductivity	20
Figure	8.	The \log_{10} relationship between calcium and specific	
		conductivity	21

Figure 9.	The log ₁₀ relationship between magnesium and specific	
	conductivity	22
Figure 10.	The \log_{10} relationship between sodium and specific	
	conductivity	23
Figure 11.	The \log_{10} relationship between potassium and specific	
	conductivity	24
Figure 12.	The \log_{10} relationship between alkalinity and specific	
	conductivity	25
Figure 13.	The \log_{10} relationship between sulfate and specific	
	conductivity	26
Figure 14.	The \log_{10} relationship between chloride and specific	
	conductivity	27
Figure 15.	The \log_{10} relationship between nitrate and specific	
	conductivity	28
Figure 16.	The \log_{10} relationship between fluoride and specific	
	conductivity	29
Figure 17.	The \log_{10} relationship between boron and specific	
	conductivity	30
Figure 18.	The \log_{10} relationship between silica and specific	
	conductivity	31
Figure 19.	The \log_{10} relationship between manganese and specific	
	conductivity	32
Figure 20.	The relationship of individual major cations, as a	
	percentage of total cations, to \log_{10} specific	
	conductivity	38
Figure 21.	The relationship of individual major anions, as a	
	percentage of total anions, to \log_{10} specific	
	anduativity	39

Figure 22.	The \log_{10} relationship between color (Hazen platinum				
	cobalt scale) and specific conductivity	47			
Figure 23.	The relationship of \log_{10} water color (absorbance at				
	320 nm in a 10-cm silica cell) to maximum lake depth	48			

The chemical composition of lakes in the north-central United States

by

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ABSTRACT

Lake waters of the north-central United States are classified into five groups, based on increasing specific conductivity and changes in ionic composition, from Wisconsin through Minnesota to North and South Dakota. The most dilute group of waters has specific conductivities less than 29 µmhos cm ⁻¹ at 25°C; the most concentrated group has specific conductivities that range from 7,000 to 73,000 µmhos. As conductivity increases all major ions increase, but there is a shift in cation dominance from Ca^{2+} to Mg^{2+} to Na^{+} , and in anion dominance from HCO_3^- to $SO_4^{\ 2-}$. This shift partly reflects a westward increase in climatic aridity, and partly a westward sequence of glacial drifts from noncalcareous to calcareous to calcareous with abundant sulfur-bearing minerals. Values of pH, K^+ , Cl $^-$, F^- , B and SiO $_2$ also show a distinct westward increase. Concentrations of NO_3^- and Mn likewise increase from east to west, but the trend is less distinct. Concentrations of Fe vary

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widely without any trend over the range of conductivity. Color, mostly from dissolved organic matter, is controlled chiefly by lake depth except for lakes with extensive peatlands in their drainage basins.

INTRODUCTION

Investigators have treated environmental controls on the surface-water chemistry of inland waters in different ways. Some have chosen areal treatments at various geographical scales from global (Clarke, 1924; Conway, 1942; Gibbs, 1970) to regional (Clarke, 1924; Gorham, 1955; Reeder and others, 1972) to local (Mackereth, 1957; Gorham, 1957a, and 1957b; Garrels and MacKenzie, 1967). Others have examined environmental factors separately with appropriate examples chosen from different regions (Gorham, 1961), discussed individual elements one by one (Hem, 1970), or provided a strongly theoretical treatment (Stumm and Morgan, 1970). This paper examines the chemistry of surface waters of lakes in the north-central states of Wisconsin, Minnesota, North Dakota, and South Dakota, classifies them into chemical categories, and relates their concentration and composition to environmental factors.

We thank Gary Glass for providing water samples from dilute lakes in the Boundary Waters Canoe Area of Minnesota, and the analytical laboratories of the U.S. Geological Survey for analyzing most of the water samples on which we report. Ronald H. Hofstetter assisted in the analysis of Minnesota waters. George H. Harrach provided valuable assistance with computer-generated graphic plots. We are grateful for suggestions and criticisms offered by Robert Hecky, William Lewis, Daniel Livingston, John Turk, and Thomas Winter.

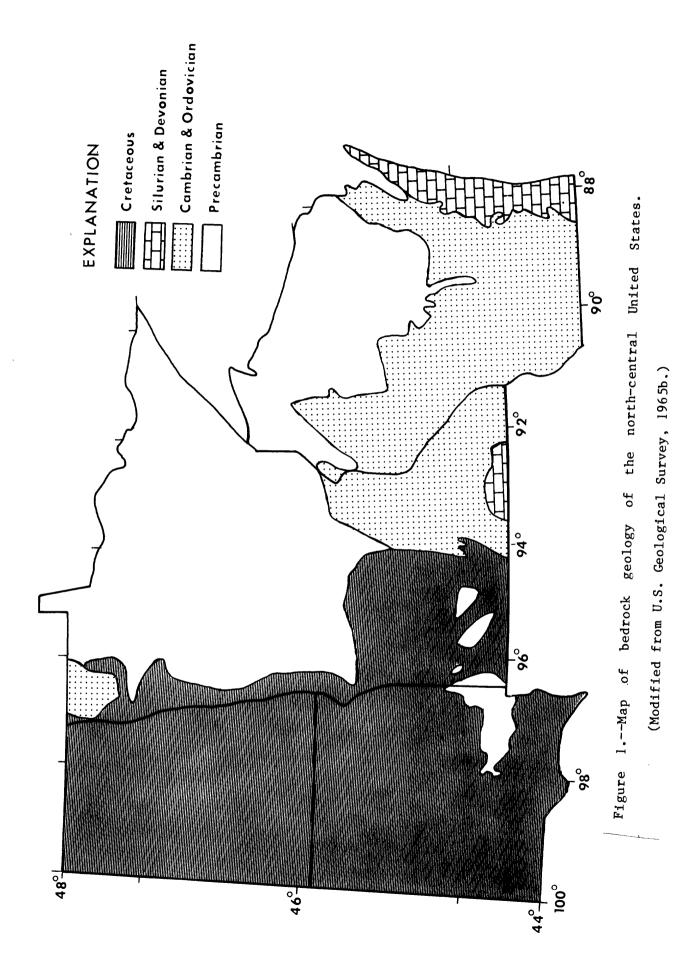
Description of the region

The study area is centered on 96°W, 45°N. It is about 1,000 km long from the Missouri River in the west to Lake Michigan in the east, and about 700 km wide from the Canadian border on the north to the Wisconsin border on the south. Elevations range from about 240 m ASL in eastern Wisconsin to about 550 m in north-central Wisconsin, northeastern Minnesota, and western South Dakota (Winter, 1974, and 1977; Petri and Larson, 1971).

Geology

Lakes in this region are mostly in glacial till and outwash or glacial lake sediments, although bedrock basins in crystalline igneous and metamorphic rocks are common in northeastern Minnesota and occur occasionally elsewhere.

The exposed bedrocks in northeastern Minnesota and northern Wisconsin are igneous Precambrian granite, gabbro, diabase and basalt, together with metamorphosed igneous and sedimentary rocks (Fig. 1, Winter, 1974, and 1977; Poff, 1970). Consolidated Paleozoic sandstone, dolomite, and limestone underlie much of the southern half of Wisconsin and southeastern Minnesota. Poorly consolidated Cretaceous shale is common in western Minnesota, except in the midwestern part where Precambrian granites and quartzites are at or near the land surface (Winter, 1974). Poorly consolidated Cretaceous and Tertiary shale, siltstone and sandstone predominate in the Dakotas (Sloan, 1972; Winter, 1977).



Glacial drift overlies most of the bedrock, and includes ground and end moraines, outwash deposits, and glacial lake sediments. Glaciers brought calcareous gray and buff colored drift into the region from the northwest, and non-calcareous red drift from the northeast. The thickness of drift in areas of large end-moraines in northwestern Wisconsin, southwestern Minnesota and the Dakotas may be as much as 150 m (Winter, 1974, and 1977).

Groundwaters

several types of groundwaters based on water chemistry (Winter, 1974, and 1977). Dilute calcium-magnesium bicarbonate groundwaters with less than $250 \text{ mg liter}^{-1}$ of total dissolved solids are common in much of Wisconsin and Minnesota, whereas the groundwaters in western Minnesota and the Dakotas are of diverse other types, including calcium-magnesium sulfate, sodium bicarbonate, sodium chloride and sodium sulfate. These groundwaters may have concentrations of total dissolved solids as high as 3,000 mg liter-1 in the Dakotas. The saline calcium-magnesium sulfate groundwaters are derived from substrates rich in gypsum and iron sulfide that were deposited by glaciers moving over Cretaceous and possibly Triassic sedimentary rocks. The sodium bicarbonate groundwaters are usually deep and products of exchange. Groundwaters dominated by sodium chloride are common in Cretaceous and Paleozoic bedrock aguifers in the Dakotas. Groundwaters rich in sodium and sulfate are believed to be caused by the mixing of sulfate-rich waters from glacial drift with waters rich in sodium chloride in underlying Cretaceous sedimentary rocks, or by cation exchange in clayey deposits. All of these saline groundwaters may move for long distances before surfacing to influence lake-water chemistry (Winter, 1974, and 1977).

Climate

Northeastern Minnesota and much of Wisconsin have a positive balance of precipitation over evaporation, whereas western Minnesota and the Dakotas have a distinct negative balance (Bright, 1968; Petri and Larson, 1971). The range is from 10-cm excess precipitation in northeastern Minnesota to a 50-cm deficit in the region of the Missouri River (Winter, 1976, and 1977). Mean annual temperature ranges from about 3°C in the north to 8°C in the south (Bright, 1968).

Vegetation

Northern Wisconsin and northeastern Minnesota are covered by mixed coniferous-deciduous forest. Deciduous forest predominates in southern Wisconsin, and as a band westward of the mixed forest, narrow in the northwest and broadening toward southeastern Minnesota. The Dakotas east of the Missouri River are covered by cultivated prairies, which extend narrowly into northwestern Minnesota and broadly across the southernmost part of the state. A generalized vegetation map is presented by Wright (1969).

Sources of data

In selecting data on ionic composition for this report we have excluded waters in which total cations and total anions were not within 5% of one another, except for very dilute samples (specific conductivity less than 29 μ mhos cm⁻¹ at 25°C) for which differences up to 10% were accepted (and only 18 of more than 50 lakes met the criteria). Most of our data for Wisconsin came from Poff (1967); the remainder (13 very dilute waters) were collected by us and analyzed by the U.S. Geological Survey. Many Minnesota samples were collected and analyzed by us, many more analyses are from Maderak (1963), some northern dilute waters were collected by Gary Glass of the U.S. Environmental Protection Agency and were analyzed by the U.S. Geological Survey, and a few analyses are from Bright (1968) and Tarapchak (1973). The data for the Dakotas are from Petri and Larson (1971), Mitten and others (1968), and the U.S. Geological Survey (1964, 1965a, 1966, 1967, 1968 and 1969). Most samples were analyzed by the standard methods of the U.S. Geological Survey (Rainwater and Thatcher, 1960; Brown and others, 1970). Our own Minnesota samples were analyzed by the techniques of Mackereth (1963).

Most of the data for Wisconsin and Minnesota lakes represent analyses of single samples collected at various times throughout the ice-free season, whereas many of the data from the Dakotas are averages of analyses of samples collected at several times during the ice-free season and over more than one year. The very considerable seasonal and annual variations of chemical composition in the western lakes are controlled by variably severe and lengthy droughts, and have been examined by Mitten and others (1968).

We have compiled measurements of specific conductivity -- closely correlated with salinity (Fig. 6) -- in 1,133 samples, and analyses of major ions -- Ca^{2+} , Mg^{2+} , Na^+ , K^+ , alkalinity, SO_4^{2-} , $C1^-$ -- in 217 samples. Many of the latter samples have also been analyzed for additional components, including pH, NO_3^- , F^- , B, Fe, Mn, SiO_2 , and color. The results of the analyses are in Appendix I.

CHEMICAL CLASSIFICATION OF SURFACE LAKE WATERS

An examination of the data for specific conductivity, taken together with data on ionic composition and surficial geology, allows construction of a chemical classification of lake waters in the north-central United States. Figure 2 shows a frequency distribution of specific conductivity (at logarithmic intervals) in all 1,133 lakes. It is evident that the distribution contains four modal groups that overlap but can be separated at approximately 28, 141, and 7,079 $\mu mhos$. Figure 3 shows separate frequency distributions for lakes in Wisconsin, Minnesota and the Dakotas that suggest another boundary at 501 $\mu mhos$, marked by the slight overlap of Wisconsin and Dakota lakes and by a "shoulder" on the middle Minnesota group. The reality of this boundary is confirmed by the changes in ionic proportions shown in Figs. 20 and 21. Five lake groups can thus be distinguished, and will be numbered I to V in order of increasing conductivity.

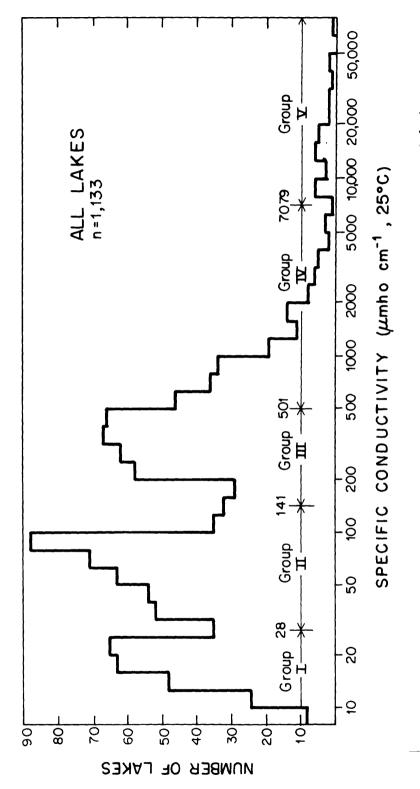
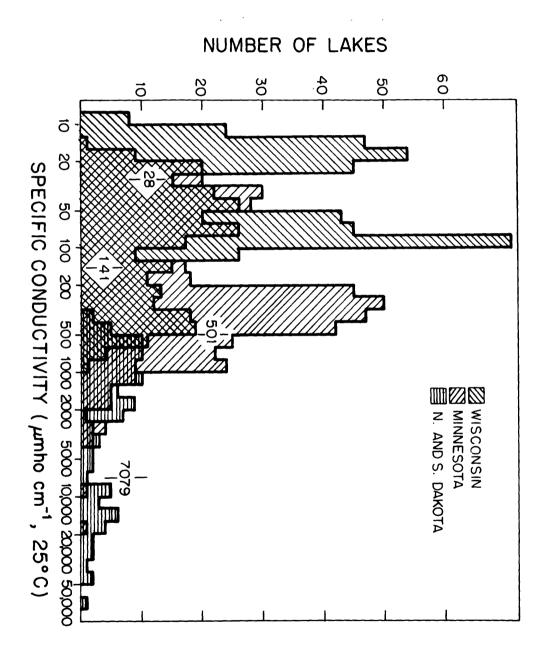


Figure 2. --Frequency distribution of specific conductivity at logarithmic futervals for 1,133 lakes.

Figure 3.--Frequency distributions of specific conductivity at logarithmic intervals for 1,133 lakes in Wisconsin, Minnesota, and the Dakotas.



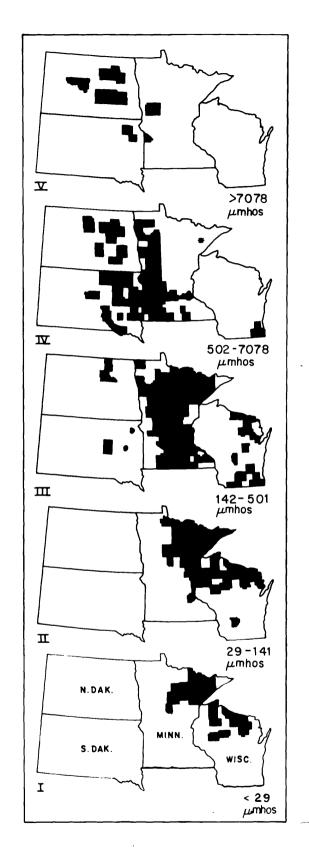


Figure 4. -- The geographical distribution (by county) of lakes in the north increasing conductivity. Group IV asterisk in northcentral Minnesota marks in order of Lake Manganika, partly filled by mines spoil. (A to grouped (I central U.S.A.,

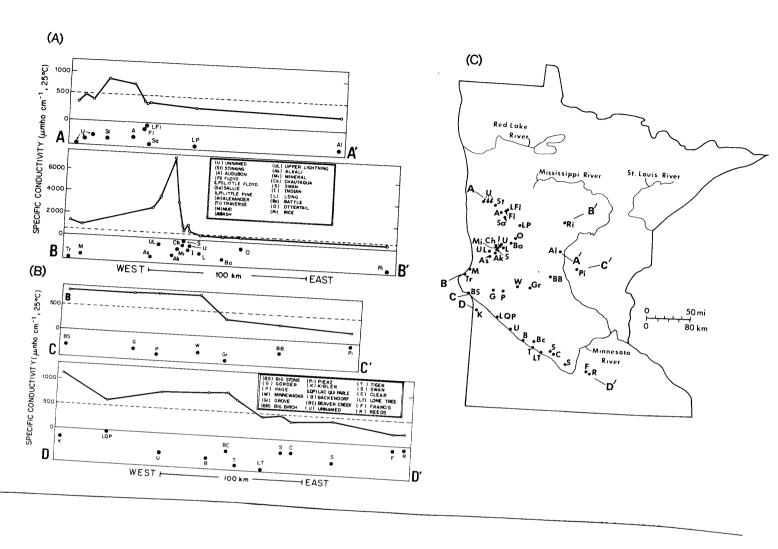


Figure 5.--Belt transects of specific conductivity in lakewaters of western Minnesota. A. northern transects. Two В. Two southern transects. Map locations of the four transects. C. The dashed lines in Fig. 5A and 5B separate lakes of group III (below) and group IV (above). The dots within the rectangles in Fig. 5A and 5Bshow the geographic positions of the lakes sampled within the belt transects.

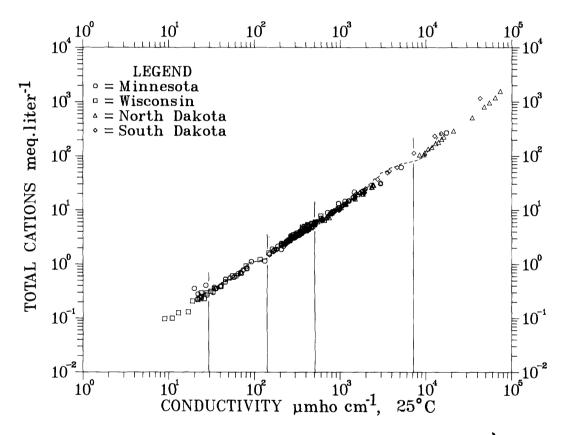


Figure 6.--The log10 relationship between total cations and specific conductivity. Vertical bars mark the separation of lake groups. For this and following figures, the dashed line is 21-point, weighted, moving-average of the raw data. Weighting was done according to the equation:

average value =
$$\frac{11 \quad \sum_{i=1}^{\infty} ix + \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} ix}{120}$$

The group I lakes are small, with more than half less than 20 ha and 80% less than 100 ha (Juday and Birge, 1941; Glass and Loucks, 1980). They are found on coarse, non-calcareous sand and gravel in northern Wisconsin and Minnesota (Fig. 4). Some occur in watersheds where much of the surface consists of bare, acidic igneous rock. Many have small drainage areas and no outlets, and have been designated "seepage lakes" by Juday and Birge (1933, and 1941) and "perched lakes" by Hawkinson and Verry (1975) to distinguish them from "drainage lakes" with outlets. Many others are headwater lakes. The waters of group I lakes are derived largely from rapid surface runoff and the most dilute among them are close to rain water in total ionic concentration. Table 1 provides representative analyses of both rain and extremely dilute lakewaters.

Group II lakes also occupy drainage basins in noncalcareous substrates in northern Wisconsin and Minnesota (Fig. 4), but many of the lakes are larger and have active outlets. Their drainage basins generally have deeper and more weathered soil profiles, and the waters therefore have higher contrations of dissolved solids.

Our frequency distributions (Figs. 2 and 3) are somewhat biased at low conductivity by an unusually large number of samples from northeastern Wisconsin. However, within that area alone the boundary between group I seepage and group II drainage lakes is clearly evident at about $28 \mu mhos$ (see Fig. 6 of Juday and Birge, 1933).

Group III lakes are on calcareous substrates predominantly in Minnesota but also to some extent in Wisconsin and the Dakotas (Fig. 4). All but the most dilute of those investigated in Minnesota are actively depositing marl in their profundal sediments (Dean and Gorham, 1976; Megard, 1968). The exceptions are a few lakes on the Anoka sand plain north of Minneapolis, where weathering profiles are deep and the surface horizons of the very sandy soils are now substantially depleted of calcium carbonate.

Table 1.--The volume-weighted mean ionic composition of atmospheric

precipitation in northeastern Minnesota, compared with the composition of the

four most dilute group I lakes (in Wisconsin)

	Rain, Hovland	d, Minn. ¹	Mean, 4 dilute lakes, Wi
	meq liter ⁻¹	meq %	meq 1 iter $^{-1}$ meq $\%$
H ⁺	0.0215 ²	22	0.005034
Ca ²⁺	0.0200	20	0.066356
1g ²⁺	0.0108	11	0.026722
Na ⁺	0.0061	6	0.00333
C ⁺	0.0033	3	0.017915
νн ⁺ ₄	0.0371	38	not done
Total cations	0.0988		0.1192
alkalinity	nil	0	0.025022
30 ₄ ²⁻	0.0394	46	0.074564
21-	0.0262	30	0.016214
10 ₃	0.0207	24	0.00
Total anions	0.0863		0.1157

 $^{^{\}mathrm{l}}$ Munger (1981), University of Minnesota. Chloride values are too high.

² pH 4.67.

 $^{^{3}}$ pH 5.30.

Group IV lakes occur chiefly in western Minnesota and the Dakotas (Fig. 4), although a few lakes in southeastern Wisconsin have conductivities above 501 µmhos. These probably represent the more saline tail of the distribution of group III lakes overlapping the distribution of group IV lakes, just as the few group III lakes in the Dakotas probably represent an overlapping dilute tail of the distribution of group IV lakes (Fig. 3). Lakes in group IV occur on calcareous substrates, but these substrates (mostly Cretaceous shales) are rich in the sulfur-bearing minerals gypsum and pyrite. As a result, sulfate increases sharply in these lake waters with increasing conductivity, and dominates strongly over bicarbonate and carbonate in the most concentrated waters.

The westward increase in climatic aridity is the main cause of the increase in conductivity between group III and group IV lakes, and also contributes to the shift of ionic dominance toward sulfate as marl is precipitated from increasingly concentrated bicarbonate waters during active photosynthesis in summer (Megard, 1968). This group boundary must also mark a change in geological substrate, or a different source of groundwater input (Winter, 1974), as can be seen in Fig. 5 which shows four belt transects of specific conductivity in lakes from east to west in western Minnesota. If the boundary between group III and group IV lakes is the result solely of a gradual climatic shift in the balance between precipitation and evaporation, a continuous westward increase of specific conductivity (and salinity) would be expected. In fact there is a sharp discontinuity between group III and group IV lakes (also observed on four other transects), which strongly suggests that a geological boundary has been crossed or a different source of groundwater The second most northerly transect appears to cross a lobe of drift marked by highly saline group IV waters, with conductivity declining again westward to that characteristic of group III waters.

Group V lakes are highly saline. Their waters are dominated by sodium and sulfate ions and show marked fluctuations in concentration with periods of drought and precipitation. The most saline lakes may precipitate hydrated sodium sulfate (mirabilite) during the winter (Mitten and others, 1968; Rawson and Moore, 1944). Sloan (1972) has noted that the most saline potholes in North Dakota occur in glacial outwash deposits at low elevation.

CONCENTRATIONS AND IONIC PROPORTIONS

The waters in groups I to V exhibit striking differences both in their ionic concentrations and in their proportions of cations and anions.

Total cations and anions

Total cations range from 0.098 meq liter⁻¹ in northern Wisconsin to 1,570 meq liter⁻¹ in N. Dakota; total anions range from 0.095 meq liter⁻¹ to 1,580 meq liter⁻¹ respectively. The logarithmic relationship between total cations (and total anions) and conductivity is approximately linear (Fig. 6), but the ratio of conductivity to ion concentration decreases from about 100:1 in the most dilute waters to an average of 54:1 in the six most concentrated waters. In the middle range of group III lakes the ratio of conductivity to ion concentration is about 89:1. The decline of the ratio with increasing conductivity is owing to lesser dissociation of the dissolved salts, which outweighs a shift of dominant anion from bicarbonate (with a low equivalent conductivity of 44 μ mhos meq⁻¹ liter⁻¹ at 25°C) to sulfate (with a high equivalent conductivity of 74 μ mhos meq⁻¹ liter⁻¹; Brown and others, 1970).

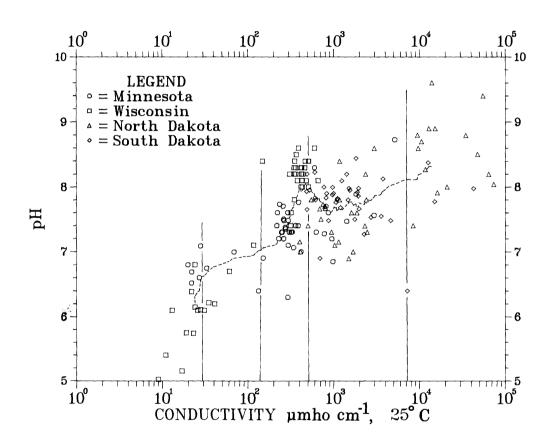


Figure 7.--The relationship between pH and \log_{10} and specific conductivity.

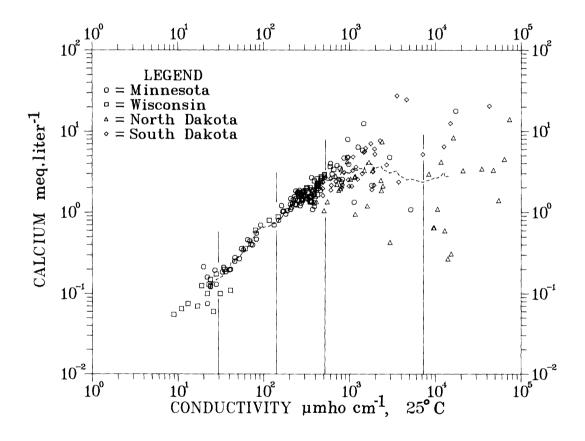


Figure 8.—The \log_{10} relationship between calcium and specific conducitivty.

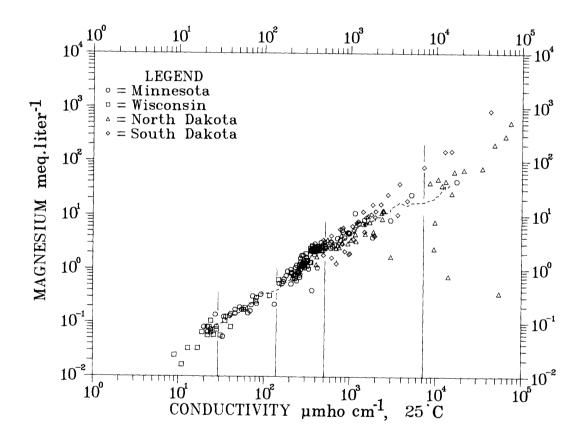


Figure 9.--The \log_{10} relationship between magnesium and specific conductivity.

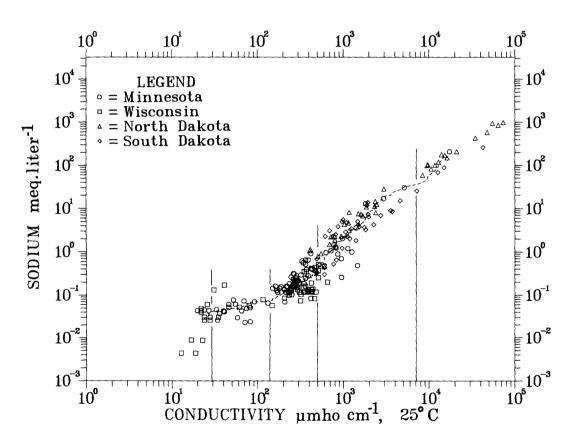


Figure 10.—The \log_{10} relationship between sodium and specific conductivity.

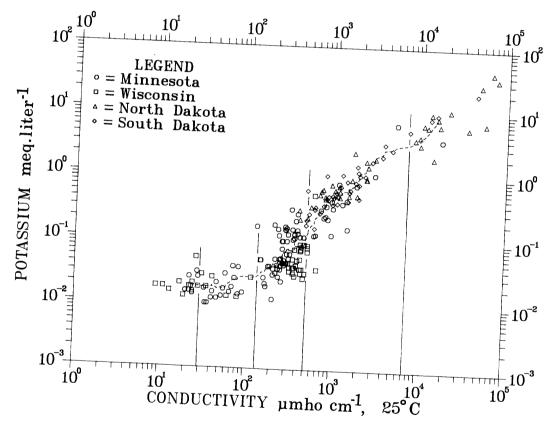


Figure 11.--The \log_{10} relationship between potassium and specific conductivity.

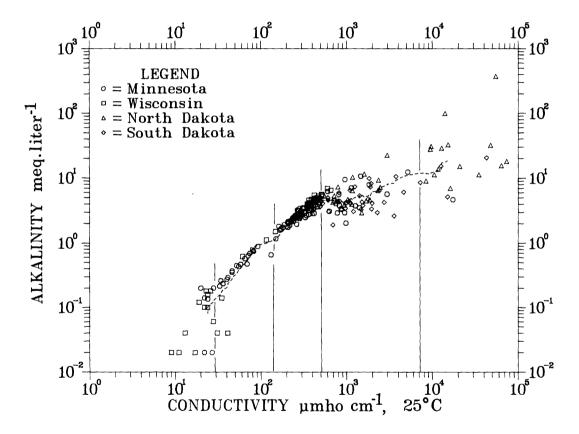


Figure 12.—The \log_{10} relationship between alkalinity and specific conductivity.

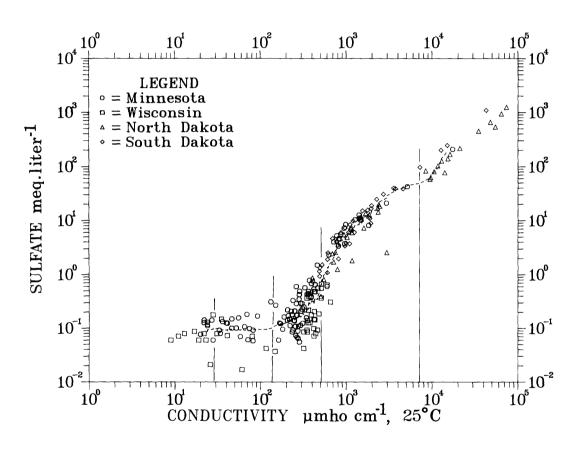


Figure 13.--The \log_{10} relationship between sulfate and specific conductivity.

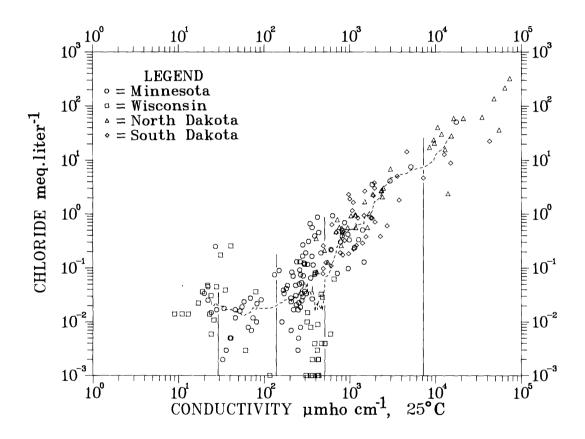


Figure 14.--The \log_{10} relationship between chloride and specific conductivity.

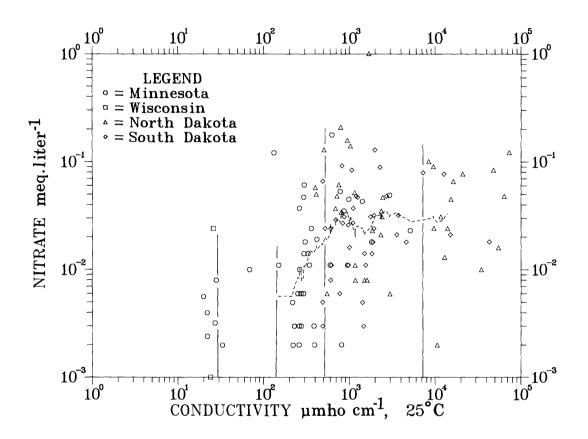


Figure 15.--The \log_{10} relationship between nitrate and specific conductivity.

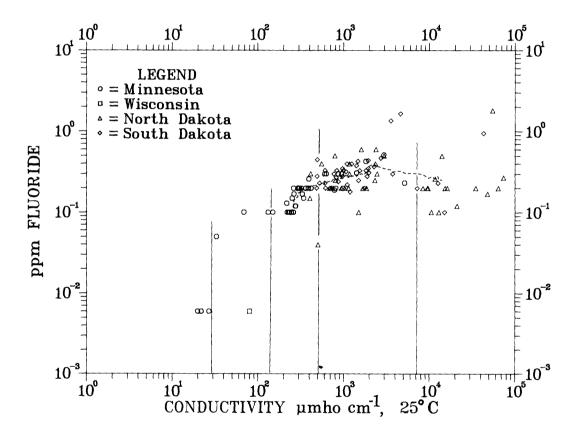


Figure 16.--The \log_{10} relationship between fluoride and specific conductivity.

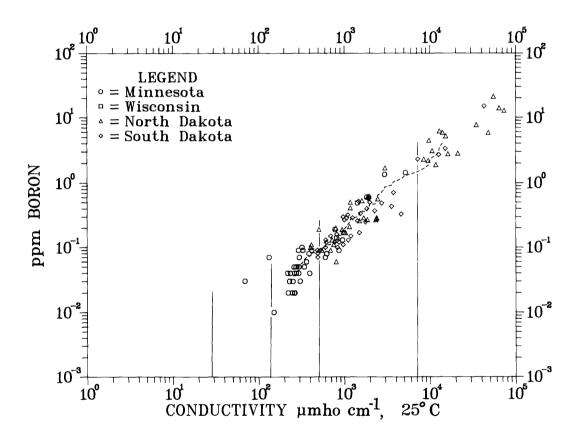


Figure 17.-- The \log_{10} relationship between boron and specific conductivity.

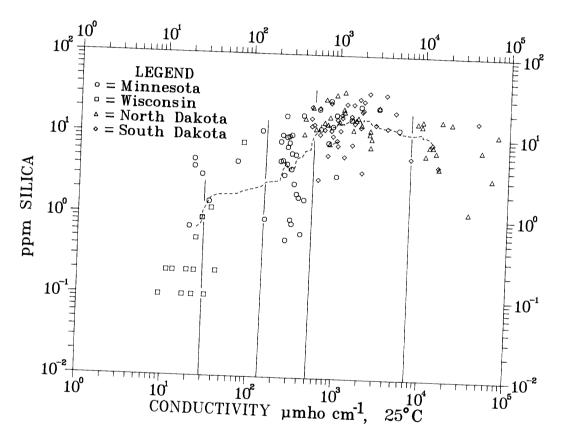


Figure 18.--The \log_{10} relationship between silica and specific conductivity.

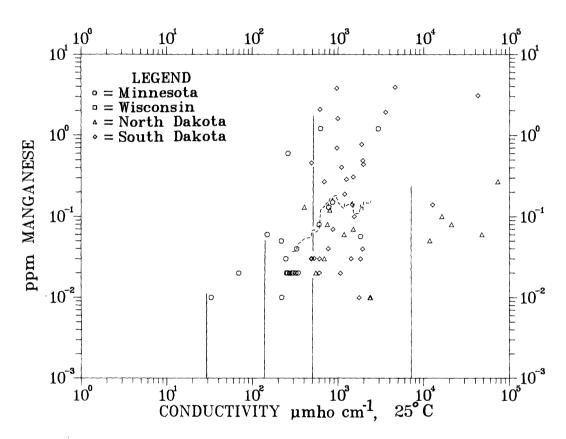


Figure 19.--The \log_{10} relationship between manganese and specific conductivity.

Trends in ionic concentration

Variations in concentrations of dissolved substances relative to specific conductivity of the waters are shown in figures 7 to 19.

Values of pH (Fig. 7) increase as conductivity increases. Group I waters are distinctly acid to neutral; group II waters are faintly acid to neutral. The range of pH of lakes on the calcareous substrata in groups III to V is from slightly acid to very alkaline; the highest pH values (above 9) occur in saline group V waters.

Calcium concentration (Fig. 8) shows a close relationship to conductivity in groups I to III, rising steadily from a minimum of about 0.05 meq liter⁻¹ to about 2.2 meq liter⁻¹ at the group III/IV boundary. Thereafter calcium concentration shows little further increase and little relationship to conductivity, presumably because above about 2 meq liter⁻¹ the waters are supersaturated with calcium ions and carbonate ions so that precipitation of marl occurs and reduces the relative importance of calcium among the dissolved ions. Dean and Gorham (1976) showed that calcium carbonate in profundal sediments of Minnesota lakes is restricted to those lakes which have a total cation concentration in the surface waters of more than 2 meq liter⁻¹, which is equivalent to a calcium ion concentration of about 1 meq liter⁻¹ and a specific conductivity of about 190 μmhos.

The relationship between magnesium concentration (Fig. 9) and conductivity is somewhat similar to that of calcium concentration. However, it continues to rise with increasing conductivity from group I to group V, and only a few saline waters show evidence of marked depletion of magnesium owing to precipitation as carbonate.

The concentration of sodium (Fig. 10) is very low in the most dilute Wisconsin waters of group I. Sodium concentrations increase sharply with increasing salinity — and presumably increased weathering soil minerals — to the boundary with group II. Sodium increases very little within group II because the salinity increase there is dominated by the leaching of calcium and magnesium from noncalcareous soils. Throughout groups III to V the sodium concentration increases steadily with increasing conductivity reflecting the accumulation of sodium salts in arid soils.

The concentration distribution of potassium (Fig. 11) resembles that of sodium, except that the most dilute group I waters have potassium concentrations similar to those of group II. In groups III to V, potassium concentration increases steadily with increasing conductivity.

The concentration distribution of alkalinity, the sum of bicarbonate and carbonate anions (Fig. 12), is similar to that of calcium, increasing steadily with increasing conductivity to the group III/IV border, after which the rate of increase becomes much less -- and the relationship less close -- as marl is precipitated and sulfate gradually replaces bicarbonate as the dominant anion.

The concentration distribution of sulfate (Fig. 13) resembles that of the cation potassium, showing little change in concentration from the most dilute to the most concentrated waters on non-calcareous substrates (groups I and II). The concentration of sulfate in lakes with calcareous drainage basins increases steadily with increasing conductivity, the increase being most rapid in the more dilute waters of group IV.

The concentration of chloride (Fig. 14) is close to or at the limit of detection in many waters from groups I to III, and increases sharply as the lakes of group IV are reached.

Nitrate concentration (Fig. 15) shows little relationship to conductivity, but there is a tendency for low concentrations in groups I and II on noncalcareous substrates with relatively little agriculture, an increase in group III where agriculture is important, and little change across the boundary of group IV and beyond in the cultivated prairie regions.

Analyses for fluoride (Fig. 16) are few in the dilute waters of group I and II where the fluoride concentration is low. Fluoride concentrations tend to rise with increasing conductivity up to the boundary between groups III and IV and then level off in groups IV and V.

Boron (Fig. 17) is usually below detection limits in dilute waters. In groups III to V on calcareous substrates, however, the concentration of boron shows a close positive correlation with conductivity.

Silica (Fig. 18) is very low in group I lake waters, among which the most dilute consist of rain-water little altered by addition of materials from soil and rock weathering. The concentration of silica increases in groups I through III as weathering products of silicate minerals are added to lake waters. It then levels off, with a slight tendency to decline in the saline waters of group V.

Iron, with few analyses in groups I and II, shows no relationship to conductivity. The concentration of iron ranges from 0.01 to 0.7 ppm and is probably controlled by redox conditions in surrounding soils and littoral sediments, as well as the degree to which sediments are resuspended in the water column by turbulence, especially in shallow lakes. Waterlogged, peaty drainage basins may contribute substantial amounts of iron to some lakes, probably chelated by dissolved organic matter.

Manganese concentration (Fig. 19) also has little relationship to conductivity, and for the same reasons as iron. However, waters of group II (with only two samples) and III tend on average to be lower in manganese than those of groups IV and V.

Trends in ionic composition

Although most dissolved materials increase in concentration with rising conductivity, their proportions relative to one another and to total ions change radically owing to differences in mineral weathering and evaporative precipitation. This appears very clearly from an examination of their percentage contributions to total cations or total anions, as seen in Figs. 20 and 21.

Calcium (Fig. 20) on average accounts for half or more of total cations in waters of group I and II lakes on substrates mapped as non-calcareous, and also in the more dilute group III lakes on calcareous substrates. As conductivity increases and calcium carbonate precipitates, calcium decreases to less than 10% of total cations in saline group V waters.

Magnesium (Fig. 20) shows a different and less clear relationship to conductivity. On average it accounts for about 30% of total cations in group I and II waters, increases to about 50% in the more concentrated group III waters because calcium carbonate precipitation reduces the calcium concentration, and then declines again (but with great variability) to about 30% in saline group V waters as sodium becomes the dominant cation.

Sodium (Fig. 20) is variable in dilute waters, and declines in importance as calcium and magnesium are weathered from non-calcareous substrates and are added to the more concentrated group II waters. Sodium remains proportionally low in the group III lakes on calcareous substrates, and then increases rapidly once the sulfur-bearing substrates of lakes with group IV waters are reached. Sodium is clearly the dominant cation in the most saline waters of groups IV and V.

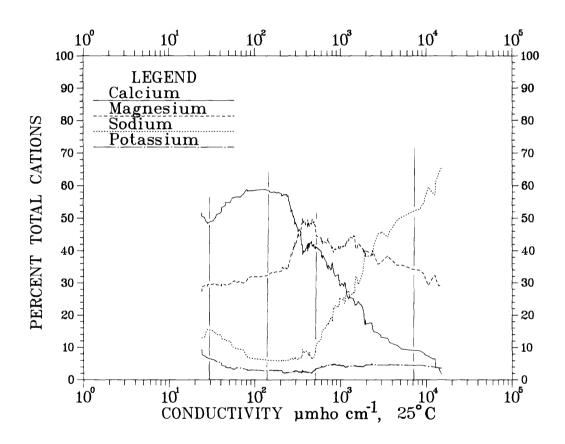


Figure 20.--The relationship of individual major cations, as a percentage of total cations, to \log_{10} specific conductivity.

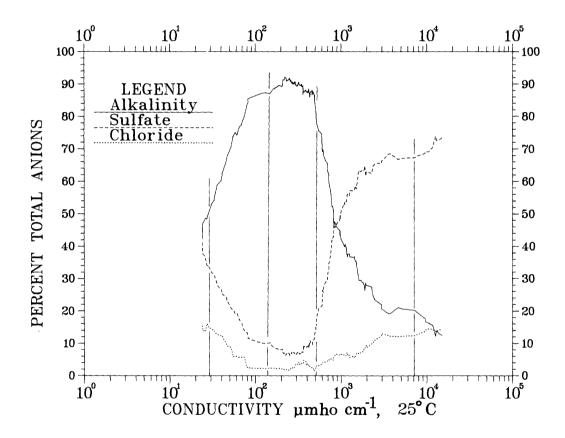


Figure 21.--The relationship of individual major anions, as a percentage of total anions, to \log_{10} specific conductivity.

Potassium (Fig. 20) is the least concentrated of the major cations and is most abundant proportionally in dilute group I waters. It declines in proportion to other cations through groups II and III, increases to slightly greater proportions in group IV, and tends to decline slightly in the most saline waters of group V.

Alkalinity (Fig. 21) is extremely low in many of the very dilute waters of group I, as it is in the atmospheric precipitation from which they are According to Munger (1981) precipitation (wet deposition only) is distinctly acid in northern Minnesota, with a mean volume-weighted pH of 4.67 At Itasca State Park in northwestern Minnesota the mean pH is at Howland. 5.00; at the Tewaukon Wildlife Refuge in southeastern North Dakota the mean pH However, as rainwaters accumulate ions through dissolution of noncalcareous soil minerals, they are enriched in bicarbonates of calcium and magnesium and are transformed into group II waters. Group II waters are increasingly dominated by bicarbonate as they become more saline. Group III Waters in lakes on calcareous substrates are strongly dominated by their alkalinity, which averages close to 90% of total anions. Group IV waters become more saline westward as they drain calcareous substrates rich in sulfur-bearing minerals, and this -- combined with the precipitation of carbonates -- results in a striking proportional decline of alkalinity in group IV waters, from about 90% of total anions near the group III/IV boundary to about 20% of total anions near the group IV/V boundary (Fig. 21). The proportional decrease in calcium and increase in magnesium, in response to precipitation of calcium carbonate, occurs within group III waters at a conductivity well below the conductivity at which alkalinity declines and sulfate increases (compare Figs. 20 and 21). As mentioned earlier, the critical empirical boundary for precipitation of calcium carbonate, based both

on the presence of calcium carbonate in the sediments (Dean and Gorham, 1976) and on the water chemistry (Fig. 20) is at a specific conductivity of about 190 μ mhos (about 2 meq liter⁻¹ total cations). Between this empirical boundary and the boundary between group III and group IV waters, the Mg:Ca ratio increases but these two cations are clearly dominant; a major change does not occur until the group III/IV boundary when both sodium and sulfate increase markedly to become the dominant ions in the more saline group IV waters.

Sulfate as a percentage of total anions (Fig. 21) is a mirror-image of alkalinity. Sulfate accounts for more than 60% of total anions in some group I waters, and declines sharply as alkalinity increases in group II waters. In the bicarbonate waters of group III lakes on calcareous substrates, sulfate is commonly less than 10% of total anions. Group IV waters are greatly enriched by drainage from substrates with abundant sulfur-bearing minerals. In the most concentrated group IV waters, sulfate accounts for about 65% of total anions; even higher percentages are observed in the saline group V waters.

Chloride (Fig. 21) dominates three dilute waters on non-calcareous substrates, where it probably comes from road salt. In general chloride is not abundant, and it declines from about 15% of total anions in group I waters to less than 5% in group III waters. Thereafter the chloride concentration increases again to about 15% in the saline waters of group V.

Nitrate is proportionally most abundant in group I waters, and declines to very slight importance in the most saline group V lakes. Fluoride is likewise proportionally most significant in the dilute waters of group I and II lakes. It declines steadily in importance as conductivity increases. In contrast, boron does not change proportionally as conductivity increases from the group III to the group V waters; it is rarely detectable in the waters of lakes on noncalcareous substrates. Silica tends to be proportionally least abundant in both the extremely dilute group I and the strongly saline group V waters, where weathering products of silicate minerals contribute least to salinity.

Q-mode factor analysis

An independent, objective confirmation of the general aspects of the lake classification and an examination of relationships among variables were obtained by Q-mode factor analysis. The computer program used for the factor analysis was the CABFAC program of Klovan and Imbrie (1971). The \log_{10} data for each of the four major cations and three major anions in 209 lakes were scaled to range from 0 to 1 so that those variables with larger means and variances would not determine the outcome of the analysis.

After varimax rotation, 93% of the variance in the scaled data could be accounted for by only two factors. A plot of varimax factor loadings from factor 1 versus conductivity was similar to the plots of proportions of calcium and alkalinity for lakes in groups I through III and the plot of proportions of Mg for lakes in groups IV and V (Figs. 20 and 21). A plot of varimax factor loadings from factor 2 versus conductivity was similar to the plot of proportions of sulfate (Fig. 21).

The factor loadings from the 0-mode analysis can be thought of as composite variables, so that the original seven variables have been reduced by the factor analysis to two factor loadings, each expressing some compositional attribute of water chemistry based on a synthesis of several measured variables. Correlation analyses among the factor loadings and the original seven measured ions show that factor 1 is mainly a measure of calcium and alkalinity with a minor contribution from magnesium. Factor 2 is mainly a measure of sodium, potassium, chloride, and sulfate.

Q-mode factor analysis confirms in a general way the 1ake specific conductivity classification obtained from and the chemical characteristics of each of the five water chemistry groups. However, the Qmode analysis recognizes only two main lake groups, one with calcium bicarbonate waters and a second with sodium, potassium, chloride, and sulfate waters; it is not capable of resolving the details of the classification we have presented. Also, the Q-mode analysis gives no indication of the details of inter-ionic associations that are particularly evident in the plots of proportions of major cations and anions (Figs. 20 and 21).

Temporal variability in concentration and composition

Lakes in the arid climate of western Minnesota and the Dakotas are particularly liable to fluctuations in concentration and composition, and the samples taken at extreme high and low water can sometimes have conductivities (and compositions) so different as to place them in different lake groups. For instance, Sully Lake near Onida, South Dakota, had a conductivity of 155 μmhos at 25°C on 7 April 1960 and 4,800 μmhos on 19 November 1959 (Petri and In late 1959 the conductivity of Sully Lake would have Larson, 1971). classified it as high group IV; in the spring of 1960 it received a great deal of dilute inflow and rose more than 3 m, which changed it to low group III. By April 1961 the water level had declined enough so that the lake crossed the conductivity boundary into group IV again and remained low in group IV until A comparison of cations in the most May 1964 when analyses ceased. concentrated and the most dilute waters of Sully Lake reveals that the concentrated waters were 16-fold richer in calcium, 45-fold richer in magnesium and 119-fold richer in sodium. Comparison of anions shows a similar trend; the more concentrated waters were 9-fold richer in alkalinity, 84-fold richer in sulfate, and 119-fold richer in chloride.

Unusual situations

Certain lakes are unusual because of natural circumstances. For instance, the group IV water of Elk Lake in Grant Co., Minnesota, has an exceptionally high ratio (>7) of magnesium to calcium, and the lake appears to be forming dolomite in its sediments as a diagenetic alteration of high-magnesium calcite (Dean and Gorham, 1976). East Stump Lake in North Dakota, because of the extreme salinity of its group V water, precipitates mirabilite (Mitten and others, 1968).

There are also regional differences between the saline group V lakes of North and South Dakota. Waters in North Dakota are generally richer in sodium and chloride, and to a lesser degree in alkalinity, than those in South Dakota. The concentrations of calcium, magnesium, and sulfate are generally higher in lakes of South Dakota. Presumably these differences reflect the influence of different types of groundwater (Winter, 1974).

Pollution may also shift a lake into a higher conductivity group. Lake Manganika in the Iron Range of northern Minnesota has group IV water rich in sulfate (Maderak, 1963), and lies far to the east of other group IV waters (Fig. 4). The reason is that a large part of the lake has been filled in with mine spoil. Some lakes such as Farquar Lake in Dakota Co., Minnesota, are strongly polluted, as indicated by a nitrate concentration of 7.5 ppm on October 1961. Big Stone Lake at Ortonville, Minnesota, also has been polluted with nitrate; nitrate levels range up to 9 ppm because of agricultural drainage. A few group III lakes in the vicinity of Minneapolis and St. Paul had, in October 1961, chloride concentrations (0.5 - 0.8 meq liter-1) somewhat higher than normal for their conductivities (300 to 400 µmhos) because roads were salted in winter.

A much greater pollution threat -- acid rain -- faces group I (and to a lesser extent group II) lakes in northern Wisconsin and Minnesota. atmospheric precipitation at Hovland in northeastern Minnesota is now 4.67 (Table 1), close to the level at which damage to lakes and their fisheries has been observed in Scandinavia (Wright and Gjessing, 1976). It is possible that a slight acidification of sensitive lakes in northern Wisconsin may already The mean pH of 18 group I lakes in Vilas and Oneida have taken place. Counties, Wisconsin, during the summer of 1979 was 5.8, as compared with a mean pH of 6.1 in the late 1920s and early 1930s (Juday and others, 1935). These lakes showed no signs of human disturbance and little change in specific conductivity over 50 years, unlike five other lakes examined at the same time where the building of roads and cottages nearby has increased the conductivity considerably. Although the decline of 0.3 pH units (a doubling of hydrogenion concentration) is statistically significant, it is by no means conclusive because the earlier analyses were made at different seasons over several years and usually by colorimetric methods -- although these measurements agreed extremely well with measurements by quinhydrone electrode. Nevertheless, these group I waters are so low in alkalinity as to be particularly sensitive to acidification, and they should be monitored with great care in the coming years.

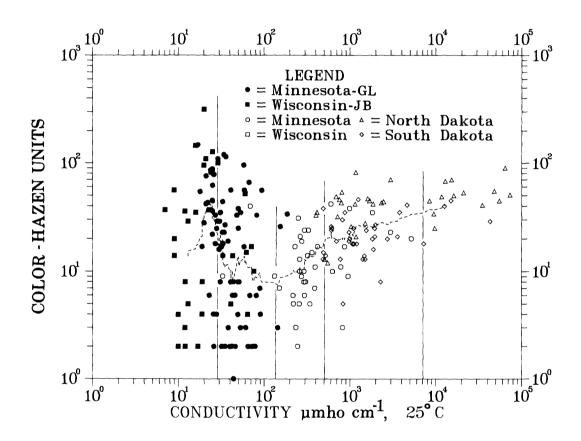


Figure 22.--The \log_{10} relationship between color (Hazen platinum cobalt scale) and specific conductivity.

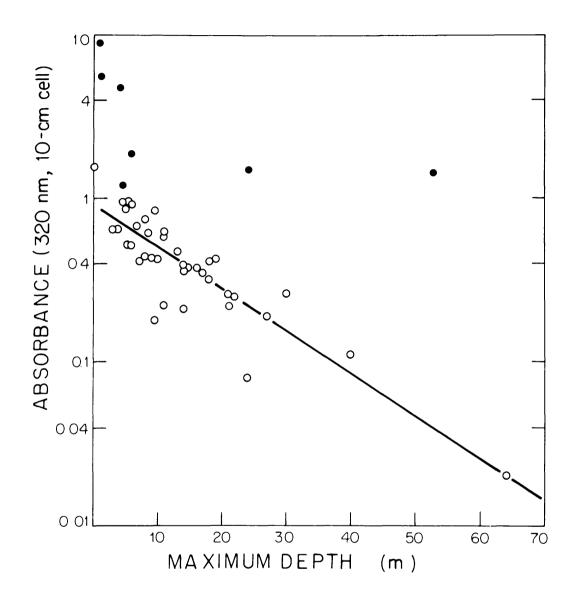


Figure 23.--The relationship of \log_{10} water color (absorbance at 320 nm in a 10-cm silica cell) to maximum lake depth. Dots represent lakes with peaty drainage; circles represent lakes with normal drainage.

COLOR

Water color -- a useful measure of dissolved organic matter (Juday and Birge, 1933) -- was not measured in most of our samples of dilute waters from group I and group II lakes; however, simultaneous color and specific conductivity data are available from these and adjacent lakes in publications by Juday and Birge (1933) and Glass and Loucks (1980). These have been treated together with our data in figure 22.

Color is extremely variable in group I and II waters, ranging from 1 to 300 Hazen units. Very low values represent surface runoff over coarse, sandy and gravelly soils with thin acid humus layers, whereas high values represent drainage from acid peat deposits. Such deposits are of little significance on calcareous substrates. The most dilute group III lakes have waters with relatively little color (averaging less than 10 units) and there is a steady increase — though not proportional to the rise in conductivity — from these waters to those of the most saline group V lakes (greater than 50 units).

Absorbance (at 320 nm in a 10-cm silica cell) was measured in 39 of the Minnesota waters as another estimate of color and dissolved organic carbon (Gorham, 1957c; Mackereth, 1963). Most of these waters came from groups II, III, and IV with one each from groups I and V. The waters were filtered quickly through a coarse paper; filtration of 10 samples (with absorbances from 0.1 to 1.6) through 0.45 μ m millipore filters removed about 5% of the color (range 1 to 11%, with no relation to amount of color).

Highly colored waters (absorbance greater than 2) were found only in lakes on peaty non-calcareous substrates. If lakes receiving peaty drainage are excluded, a very close correlation (r = -0.88) is observed between log_{10} color and maximum lake depth. The inverse relationship of color (and dissolved organic matter) to depth (Fig. 23) is probably explained by the interaction of several factors: (1) shallow lakes are more productive per than deep lakes and hence the volumetric secretion of unit volume extracellular metabolites and the release of dissolved organic matter by decomposition of dead plankton is greater in shallow lakes; (2) the ratio of sediment area to water volume is higher in shallow than in deep lakes, leading to a greater concentration of dissolved organic matter released to the overlying water by decay in the sediments, and (3) evaporative concentration per unit volume is greater in shallow than in deep lakes. Decreasing depth is probably an important factor in the increase of color (Fig. 22) from the most dilute group III lakes to the most saline group V lakes.

DISCUSSION

It is clear from our results that the chemistry of surface waters of lakes in the north-central United States -- like the chemistry of groundwaters (Winter, 1977) and of profundal lake sediments (Dean and Gorham, 1976) -- can be understood largely in terms of the interaction of climatic and geologic factors, although human influences are discernible in some lakes. Our data are in accord with -- and provide a detailed background to -- the broad generalization by Clarke (1924) that there is a pronounced shift from bicarbonate-dominated waters in the humid forests east of the Mississippi to sulfate-dominated waters that precipitate calcium carbonate in the more arid prairie regions of the west. In addition we have shown that changes in geologic substrate are also important.

Our data are broadly compatible with the model presented by Gibbs (1970) for the control of global water chemistry by atmospheric deposition, rock weathering, and the evaporation/precipitation process. He observed that the most dilute surface waters, which have ionic compositions close to rainwater, have high ratios of sodium to calcium and of chloride to bicarbonate. ratios decline sharply toward the middle range of salinity where rock weathering is the predominant source of ions, and rise again as evaporation 1eads to further ion concentration and the precipitation of calcium Generally similar relationships occur in the north-central United carbonate. States (Figs. 20 and 21), but the ratio of sodium to calcium is not nearly so high as that observed by Gibbs (1970), who included a number of rivers that are strongly influenced by atmospheric deposition of sea spray. Likewise, the ratio of chloride to alkalinity never reaches the high levels observed by Gibbs (1970) at either end of the salinity range where again sea salt plays a

predominant role. The distribution of the ratio of sulfate to alkalinity in the north-central United States is similar to the distribution of the ratio of chloride to alkalinity presented by Gibbs (1970); both are low in the middle range of salinity (Fig. 21).

Contrary to the view expressed by Bright (1968), water chemistry does not appear to be closely related to vegetation type. The boundary between the lakes of groups II and III generally runs east of the boundary between coniferous and deciduous forests shown by Wright (1969), whereas the boundary between groups III and IV is usually west of the forest-prairie boundary.

According to Hall (1972) the chemical composition of Minnesota lake waters approximately fits a model in which rainfall enriched by soil-derived carbon dioxide reacts with calcite, dolomite, gypsum, illite, and sodium feldspar at 5° C and 1 atmosphere total pressure. He suggested that the lake waters become saturated with respect to calcite at about 5 meg liter total cations (equivalent to a specific conductivity of about $450 \, \mu \text{mhos cm}^{-1}$) and with respect to calcite and dolomite at about 8.9 meg liter⁻¹ total cations (specific conductivity of about 750 µmhos). However, this does not agree with our empirical boundary (Dean and Gorham, 1976) for carbonate precipitation at 190 μ mhos (about 2 meg liter $^{-1}$ total cations). Hall also suggested that the dissolution of gypsum becomes progressively more important as salinity increases above 5 meq liter $^{-1}$ total cations, which is consistent with Fig. 13 and Fig. 21. Our data also show (Fig. 21) that sulfate begins to dominate the anions above about 10 meg liter total cations (specific conductivity of about 900 µmhos). Hall (1972) suggested further that isothermal evaporation of waters in the lakes of southwestern Minnesota should produce highly alkaline magnesium-calcium sulfate waters that he claimed were typical of the closed-basin lakes of the Dakotas. However, he did not account for the

predominantly sodium sulfate lakes that are characteristic of the most concentrated closed-basin lake waters in those states and begin to appear as salinity increases above about 30 meq liter⁻¹ (specific conductivity about 2,200 μ mhos). Our data, moreover, indicate that at concentrations where sulfate begins to dominate over alkalinity (specific conductivity about 900 μ mhos, Fig. 21), sodium is already a significant cation approaching calcium in concentration (Fig. 20).

According to Sloan (1972) the sodium sulfate waters of North Dakota do not require bedrock sources of saline water as sometimes suggested, but are the result of an evaporation sequence in which the waters are dominated successively by calcium bicarbonate, magnesium bicarbonate, calcium and magnesium sulfate, and sodium sulfate. Mitten and others (1968) noted that runoff from the Big Coulee at Church's Ferry into the markedly saline Devil's Lake chain in North Dakota is normally dominated by calcium, magnesium, and bicarbonate ions except during periods of low flow when sodium and sulfate ions predominate. As the dissolved salts in the runoff are concentrated by evaporation, the alkaline-earth carbonate minerals precipitate so that the waters stored in the chain of lakes come to be dominated strongly by sodium and sulfate ions, chloride increases markedly, and calcium decreases to only a few percent of total cations.

The work reported here does raise questions — of a kind frequently encountered — for further study by hydrogeologists, glacial geologists and soil scientists. For example, several group III lakes occur on glacial deposits mapped as noncalcareous red drift (for example, west of Mille Lacs, Minnesota (Winter, 1974). Presumably these lakes are tapping calcareous material underlying rather shallow red drift. Likewise group II lakes may occur as western outliers on deposits mapped as calcareous gray drift (for example, several lakes in Itasca State Park in northwestern Minnesota). These lakes are small and usually are found on sandy, gravelly material that has probably undergone substantial surface depletion of calcium carbonate by soil leaching. The larger lakes in the area that drain deeper weathering profiles have normal group III waters.

The boundary between group III and group IV lakes raises a very interesting hydrogeological problem. At present it is impossible to say how closely that boundary reflects mineralogical and chemical differences in the respective glacial deposits, and how far it may be influenced by regional versus local groundwater flow (Winter, 1974, and 1977).

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APPENDIX I

Specific conductivity (µmhos cm⁻¹ at 25°C), concentrations of calcium, magnesium, sodium, potassium, alkalinity, sulfate, chloride, nitrate, fluoride, and total cations in meq liter⁻¹ (epm), and concentrations of silica, iron, manganese, and boron in mg liter⁻¹ (ppm) in surface waters of 217 lakes in Wisconsin (W), Minnesota (M), North Dakota (N), and South Dakota (S). Values of pH are in relative pH units. Values of color are in Hazen units, and values of optical density are in absorbance at 320 nm in a 10-cm silica cell. Leaders (--) mean no analyses were made.

su									
opt.dens	11111		21111	1 62	188 26 11	36 143 52 149 57	53 32 35	78 47 484	18 42
color	11111	11111	11111	•	11111	11111	4	11111	e _
Н	5.02 5.40 6.10 5.15 5.75	6.80 6.52 6.69 6.39 5.74	6.15 6.80 6.10 6.60	7.09 6.11 6.10 6.75	6.22	11111	6.70	7.10	6.40 8.40 6.90
ppm-B	11111	11111	11111		11111	11111	11:011	11111	.010
nM−mqq	11111	11111	11111	1110:1	11111	11111	1 1 . 020	11111	0 0 1
ppm-Fe	11111	11111	060	1110:1	11111	11111	220	11115	.080
ppm-Si02	.100 .200 .200 .100	.700 3.900 4.800 .100	.500	.900 .900 .100 1.450	1.200	11111	4.530	7.800	11.000
tot-cat	. 0975 . 0993 . 1275 . 1319	.3558 .2260 .2800 .2231	.2550 .2415 .2980 .2300	.2680 .2928 .3159 .3020	.3549 .3610 .3870 .4000	.4700 .5240 .5550 .6100	.6130 .6680 .7010 .6780	.9234 .8490 .8250 1.1180	1.1460 1.6230 1.5340 1.9250 1.7520
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epm-T-n	00000	.0056	.0 .0010 .0240 .0032	.0080	91119	11111	0.1.01	91119	.1210
e pm-Cl	.0141 .0141 .0141 .0225 .0366	.0338 .0451 .0254 .0479	.0150 .0310 .0060 .0110	.0169 .0451 .1746 .0020	.0394 .0030 .0050 .0050	.0120 .0170 .0160 .0190	.0030 .0080 .0280 .0070	.0366 .0220 .0100 .0260	.0760
e pm-504	.0604 .0708 .0792 .0875	.0771 .1417 .1271 .0792	.1110 .1292 .1190 .0210	.0604 .1792 .0792 .0920	.1479 .1340 .1260 .1240	.1000 .1490 .1010 .1560	.0170 .1070 .1830 .0610	.0708 .0920 .0580 .1680	.3120 .0370 .2700 .0600
epm-alk	.020	.200 .020 .140 .100	.135 .100 .160 .180	.200 .060 .040 .214	. 140 . 235 . 274 . 293	.372 .354 .449 .432	.622 .572 .476 .640	.780 .746 .750 .888	.656 1.506 1.164 1.816 1.588
epm-K	.0179 .0179 .0153 .0205	.0153 .0256 .0153 .0179	.0140 .0205 .0150 .0510	.0256 .0179 .0281 .0170	. 0179 . 0100 . 0120 . 0150	.0120 .0210 .0130 .0170	.0130 .0150 .0180 .0380	.0128 .0140 .0370 .0150	.1590 .0490 .0490 .0260
epm-Na	.0 .0 .0043 .0087	.0435 .0435 .0391 .0478	.0450 .0304 .0260 .0610	.0304 .0261 .1304 .0460	.0304 .0370 .0420 .0410	.0610 .0520 .0770 .0610	.0520 .0430 .0740 .0230	.0565 .0510 .0240 .0700	.0650 .0570 .1440 .1610
e pm-Mg	. 0246 . 0164 . 0328 . 0328	.0820 .0820 .0656 .0574	. 0740 . 0656 . 1070 . 0580	. 0820 . 0738 . 0574 . 0540	.1066 .1280 .1350 .1440	. 1470 . 1730 . 1950 . 1740	.1890 .1500 .1650 .2140	.2541 .2280 .2960 .3380	. 2220 . 6340 . 5430 . 5340
ерш-Са	.055 .065 .075 .070	.215 .075 .160 .100	.122 .125 .150 .060	.130 .175 .100 .185	.200 .186 .198 .200	.250 .278 .358	.359 .460 .444 .403	.600 .556 .468 .695	.700 .883 .798 1.204 1.016
K-pmhos	9 11 13 17 19	22 22 22 33	24 24 26 27	28 28 31 33 34	335 4 4 4 4 4 1 1 4 1 1 1 1 1 1 1 1 1 1 1 1	46 46 52 55 58	61 65 69 71 74	80 82 82 92 116	132 148 150 162
County	Vilas Vilas Vilas Oneida Vilas	St. Louis St. Louis St. Louis Vilas	St. Louis Vilas Oneida Chippewa St. Louis	St. Louis Vilas Vilas St. Louis Carleton	VIIas Cook Cook Cook VIIas	Lake St. Louis Cook St. Louis Hubbard	Washburn Lake St. Louis Hubbard St. Louis	Cook Cook Hubbard Carlton Burnett	Dalota Walworth St. Louis Crow Wing
State	33333	EEZZZ	ZESSZ	ZZZZZ	32223	EEEEE	3222	EZZZZ	ZZZZZ
Lake Name	Ruth	Emerald	B1 g	Fishmouth	Nose	Wilson	Big Bassond	Trout	Farquar——————————————————————————————————

58 38 68 62 552	120 41 32	47 41 41	52	26 19 8		11111	81111	11181
11111	11001	m 2	31 5 10 13	21 6	21111	10 24 8	1 1 4 1 5 4 5 4 5 4 5 6 6 6 6 6 6 6 6 6 6 6 6 6	~!!!!
11111	7.40	7.73	7.30 7.70 7.50 7.20	7.48	7.35	6.30 7.48 7.10 7.30 8.20	7.40 7.30 7.60 7.30	7.06 8.30 7.80
11111	.040	.040	.030	.020	.040	.050	.100	050.1111
11111	.050	030	.020	0001	\$1111	<pre><0 <0 <0 <0 </pre>	.020	.020
11111	.050	.030	.030	.070	090:111	.030 .020 .030 .020	.020 .030 .010	.020
11111	8. 230 4. 750	4.830	17.000 9.400 .500 4.400	7.120	8.030	. 900 5. 930 3. 800 . 800	2.500	1.880
1.8180 1.8980 2.1590 2.2310 1.8790	2.4160 2.3040 2.1560 2.3670 2.5820	2.4710 2.5850 2.6740 2.6160 2.8300	2. 7610 2. 8260 2. 8120 2. 8890 2. 7310	2.8990 3.3820 3.1200 3.0290 3.2940	3. 0320 3. 0360 3. 1880 3. 5300 3. 2490	3.1180 3.2730 3.1340 3.2290 3.5940	3.7870 3.5560 3.5080 3.5940 3.3910	3.5640 4.0160 3.7450 4.0970 3.7100
11111	130	15115	.150	.170	1111	.200 .200 .200	.200	.150
11111	.0050	\$11\$1	.0060	.0100		.0470 .0140 .0610 .0180	1.0000.0000.000000000000000000000000000	0.00.10
.0340 .0420 .0480 .0280	.0240 .0840 .0710 .0170	.0310 .0210 .1320 .0030	.0050 .0230 .0510 .0930	.0080 .0190 .0760 .0540	.0340 .1680 .2700 .0300	.1240 .0370 .1180 .1920	.0340 .0100 .1180 .0150	.6660 .0080 .0080
.1220 .0960 .1630 .1410	.2210 .1720 .1480 .1120	.0850 .0930 .3320 .1410	.2110 .1090 .0730 .2910	.1750 .0680 .1770 .0890	.1100 .3500 .4250 .0550	.2910 .2080 .2080 .2910	.1240 .0420 .2500 .0850	.1580 .0930 .3670 .4370
1.658 1.747 1.924 2.069 1.758	2.155 2.028 1.897 2.239 2.348	2.383 2.464 2.168 2.509 2.630	2.485 2.700 2.722 2.460 1.968	2.673 3.247 2.837 2.819 3.210	2.875 2.470 2.404 3.454 2.598	2.640 2.972 2.706 2.772 3.410	3.437 3.513 3.083 3.482 2.498	2.673 4.022 3.425 3.480 3.707
.0190 .0390 .0390 .0290	.0360 .1710 .0510 .0310	.0360 .0270 .1180 .0510	.0400 .0520 .0230 .0970	.0440 .0450 .0970 .0490	.0410 .1620 .1460 .0440	.1540 .0610 .0970 .1230	.0520 .0380 .0610 .0330	.1480 .0380 .0510 .1030
.1150 .1430 .1560 .1340	.0690 .1170 .1610 .1570	.1830 .1170 .1280 .2610	.1020 .1640 .1570 .2350	.1700 .3130 .1960 .2180	.1830 .2180 .2480 .2780	.1310 .1480 .2180 .1910	.1920 .0740 .2960 .1040	.5610 .1480 .3480 .1840
.6520 .7600 .9160 .9840	.8460 .8680 .6670 .7570	.7900 .6130 1.1960 .9040	.8470 .8800 1.2350 .7070	.9880 1.3780 1.6260 1.1850 1.7960	1.1360 1.2440 1.3330 1.8200 1.1280	1,2330 1,2180 1,0690 1,3150 1,9510	1.6890 1.4480 1.1510 1.4810 1.0210	1.3580 2.4530 1.3500 2.2420 2.2300
1.032 .956 1.048 1.084 1.250	1.465 1.148 1.277 1.422 1.254	1.462 1.828 1.232 1.400 1.720	1.772 1.730 1.397 1.850 1.550	1.697 1.646 1.201 1.577 1.291	1.672 1.412 1.461 1.388 1.796	1.600 1.846 1.750 1.600	1.856 1.996 2.000 1.976 1.452	1.497 1.377 1.996 1.568
171 181 188 206 206	207 211 218 221 233	234 238 240 246 246	251 254 258 261 262	264 266 266 273 274	276 282 283 284 286	293 296 297 305 308	311 318 321 321 329	342 347 348 349 351
Anoka Anoka Anoka Isanti Isanti	Beltrami Waseca Aftkin Cass Lesueur	Crow Wing Crow Wing Steele Morrison Itasca	Itasca Itasca Hubbard Washington St. Louis	Pine Clearwater Hennepin Cass Clearwater	Cass Waseca Carver Clearwater Lesueur	Carver Beltrami Ramsey Hennepin Walworth	Ottertail Langlade Ramsey Langlade Hard	Hennepin Walworth Oconto Pope Walworth
ΣΣΣΣΣ	EEEEE	ΣΣΣΣΣ	EEEEE	EEEEE	EEEEE	EEEE	DSEBO	E 3 3 E3
Linwood	Upper Red	Pelican	Round	Pokegama	Winnebigoshish St. Olaf Lotus Itasca Clear	Prior Red Centerville Medicine Booth	Little Pine Hogiot Vadnais Speigal Louise	Minnetonka Beulah Mt. Spring Crove Pleasant

opt.dens	1 1 8 8 1	1 1 2 1 1	21111	11111	%	11111	11111	11111	11111
color	11112	11117	33 33 33	171	11111	11112	15 38 13	117 12 42 42	26 24 25 10
μф	8.40 8.30 7.40	8.20 8.50 8.10 7.40	8.60 7.76 7.15 7.00	8.30 7.00 8.00 8.20	8.30 8.10 8.00	8.30 8.40 8.10 7.93	8.20 7.65 7.40 8.40 8.00	8.40 7.95 7.80 8.60 8.30	8.23 7.83 7.80 7.30 8.10
g − md d	111100	11118,	.040	10.111	11111	11110.	.070	000.	.100 .130 .120
uW-mdd	11119		130		11111	.030	.030	.030	.020 .030 2.080 1.200
ppm-Fe	.010	.060	.070 .050 .020 .030	.020 .020 .160 .070	.010 .080 .140 	.070 .080 .070	.030 .030 .030 .130	.080 .020 .010 .340	.020 .020 .030 .030
ppm-S102	1.700	1 009:	17.400 10.250 16.000	1.600	11111	16.100	13.000 22.200 22.000	13.630 12.000 21.000	21.750 2.880 10.380 12.000
tot-cat	3.8880 4.0020 4.3840 4.3960 3.8140	4.8510 4.5900 4.1210 4.1370 4.1000	4.6000 5.0520 4.3930 4.1670	4.5810 4.2460 5.4030 4.4950 5.1600	4.4890 4.4810 4.9890 5.1200 4.8880	5.5460 4.7960 5.7410 5.0460 5.4460	5.6240 5.4460 5.4300 5.6590 5.8400	6.0950 5.9130 6.1330 7.7610 7.0600	6.3740 6.8370 6.3830 6.6600 6.5000
e bm-F			.150		11111		.450	.230	.330 .200 .300
epm-T-N	.0	0030	.0020	0.0190	00010	.00.00	.0030 .0660 .1290 .0	.0 .0240 .0060 .0	.0080 .0240 .0110 .1770
epm-Cl	.0 .0 .1670 .0270	.0020 .0010 .1150 .0	.0770 .0040 .0820 .3530	.0030 .8740 .0010 .0090	.0020 .0020 .0010 .4550	.1920 .0330 .0040 .0290	.0990 .2620 .2140 .0040	.0040 .1270 .1300 .0060	.1100 .2170 .6430 .9310
e pm-S04	.0850 .1270 .4920 .4480	.2200 .3950 .7870 .1270	.3870 .1780 .6820 .8630	.0990 .5410 .0710 .1470	.2060 .1440 .4880 .6510	1.5080 .0930 .5640 .1860	.9360 1.3400 .3950 .5580	.6710 1.5140 .8110 .6430	1.0880 1.9140 2.5440 2.3300 3100
epm-alk	3.954 3.950 3.606 3.709 2.772	4.583 4.195 3.190 4.138 3.362	4.162 4.702 3.687 2.878 3.493	4.451 2.870 5.494 4.525 4.846	4.293 4.510 4.744 3.877 4.969	3.644 4.830 5.290 4.945 4.084	4.488 3.631 4.625 5.290 5.620	5.533 4.086 5.314 6.928 6.219	4, 998 4, 592 3, 093 3, 116 6, 456
e pm-K	.0380 .0380 .1230 .1250	.0720 .0280 .2000 .0410	.1440 .0490 .1280 .2940	.0360 .1130 .0510 .0360	.0690 .0310 .0720 .0790	.1130 .0260 .0870 .0310	.2070 .5940 .2250 .0840	.0670 .2590 .3330 .4990	.3070 .3330 .1230 .0360
epm-Na	.1170 .1170 .5160 .2470	.1610 .3480 .3930 .1220	.2790 .1350 .1220 1.0660	.1170 .9140 .0830 .1350	.1910 .1220 .4130 .3960	.4440 .0830 .3740 .1170	.3220 .6920 .7830 .3700	.5090 .5050 .9140 .4570	.3000 .4310 2.2840 .9570
e pm-Mg	2.2060 2.2800 2.3770 2.7000 .4030	2.7320 2.4530 2.4440 2.1480 1.8910	2,9950 2,4530 2,4360 1,2350 1,7280	2, 3370 1, 0690 2, 6990 2, 2630 2, 3950	2.5920 2.2220 2.2880 2.6940 2.4770	3.1570 2.2470 2.5600 2.2880 2.9870	3.4980 1.8350 3.3740 2.4850 2.6170	2. 6750 2. 4690 3. 5390 3. 1520 2. 4690	3.3330 4.2380 1.6300 2.6300 2.8810
epm-Ca	1.527 1.567 1.368 1.324 2.650	1.886 1.761 1.084 1.826 1.300	1.182 2.415 1.707 1.572 1.347	2.091 2.150 2.570 2.061 2.265	1, 637 2, 106 2, 216 1, 951 2, 236	1.832 2.440 2.720 2.610 1.946	1.597 2.325 1.048 2.720 2.894	2.844 2.680 1.347 3.653 3.992	2, 585 1, 861 2, 136 2, 950 3, 383
K-pmhos	351 360 361 362 362	363 369 372 379 388	390 390 393 404 413	417 418 419 420 423	424 431 432 433 440	460 461 469 478 485	491 491 505 511 511	513 523 550 597 599	603 605 615 625 655
County	Walworth Walworth Becker Douglas Henne p in	Racine Racine Cottonwood Walworth Carver	Douglas Racine Becker Towner Benson	Walworth Ramsey Racine Waukesha Racine	Walworth Waukesha Racine Henne p in Walworth	Douglas Waukesha Racine Waukecha Day	Day Clark and Kingsbury Eddy Racine Racine	Racine Codington Benson Racine Clearwater	Day Marshall Brown St. Louis Waukesha
State	33225	33232	EBEZZ	3 2 3 3 3	33323	z è z z o	8 8 8 8 8	3 0 Z 3 E	o o o zz
Lake Name	Green	Rockland	Maple	Middle	Army————————————————————————————————————	Mina	Enemy Swim	Tichigan	Blue Dog

11211	11111	1.2111	200	11111	4	1 6	290	11111
49 19 32 46	13 11 43 54 3	30 5 17 35	9 19 23	38 20 26 18 25	18 42 82 21	13	14 13 24	47 45 35 20
7.66 6.90 7.50 7.73	8.00 7.28 7.70 7.67 7.70	7.83 7.90 7.60 7.48	7.30 7.20 8.00 7.88	6.85 7.90 7.10 7.76 7.80	7.82 7.15 8.40 7.80	7.68 8.10 8.20 7.47	7.80 6.90 7.98 7.95	7.60 7.00 7.50 7.89 8.45
.090.150	.120 .190 .200 .060	.160	.130	.170 .270 .170 .290	.130	.290	. 520 . 260 . 170	. 530 . 290 . 250 . 601
.030	.040 .130 <0 .120 <0	1150	<pre></pre>	1.600 <0 .020		.190	 .140 .070 .310	<0 <0 <0 .010 .057 .030
.050 .060 .070	.030 .070 .040 .070		.020	.060	.060	.020	.020 .060 .050 .040	.010 .040 .110 .269
14.500 11.900 28.000 13.790	5.750 8.210 17.000 8.040 27.000	25.330 11.670 13.000 9.920	32.000 18.000 15.980 8.830	3.200 7.650 15.000 11.720 18.330	16.940 21.500 35.000 20.000	5.630 24.750 17.750 15.960	8.000 12.000 24.750 14.500	16.000 17.000 29.000 23.139 13.050
7.2720 7.0170 8.9040 7.8020	8. 8740 8. 6080 9. 0180 8. 8390 9. 3210	8.5510 9.0640 9.1930 9.7020	10, 2850 10, 7060 13, 0750 11, 1670 9, 8820	10.9070 10.0540 11.0050 11.9040	12.9180 14.3690 12.6020 13.0290 13.0890	13.7120 14.7890 14.7710 17.4380 16.8670	21, 3300 15, 9800 15, 9340 17, 4040 19, 8910	19. 1570 20. 9420 22. 0550 19. 5760 22. 5600
.200 .200 .200	.300 .190 .500 .250	.330	.300	.200 .330 .200 .320	.220	.180		.600 .200 .200 .430
.0370	.0060 .0530 .2090 .0340	.0920	.0110	.0450 .0160 .1400 .0840	.0370	.0480	.0030 .0080 .0140	.0080 1.0140 .0310 .0180
.4710 .4600 .0800 .7900	.1950 .3050 .2620 .5440	.4430 .4900 .1750 .6890	.5640 .4230 .0980 .1860 2.3270	.3330 1.9120 .9310 1.1730 1.6640	.2280 .2400 .9590 .5640	.2620 .8460 .3400 .2930	.1300 .9450 1.6920 2.6870	.5640 1.0150 .8460 3.5530
2. 4500 4. 6700 4. 0200 1. 7060 2. 5750	4, 0350 5, 2460 1, 2480 3, 6840 3, 3900	1,9610 4,6700 4,5280 5,6200 5,9760	5.4700 7.2590 3.7280 7.2900 3.4010	8.3780 3.8170 4.8880 6.0110 3.7380	8.3780 6.7600 7.4360 5.9900 1.8100	9.8490 6.0800 10.3000 11.2420 12.6460	10.1600 11.2320 11.7310 9.9070 15.1170	7,3220 13,5410 15,6000 8,1790 11,4570
4.287 1.911 4.469 5.346 4.074	4.431 2.929 7.331 4.474 5.592	5.986 3.796 4.423 3.371 3.269	3.870 2.952 9.494 3.447 4.080	2.039 4.204 4.690 4.414 6.499	4.098 7.036 3.985 6.432 10.234	3.116 7.344 3.760 5.346 3.500	10.676 3.305 2.952 4.317 3.805	11.447 4.461 4.723 7.899 9.843
.5170 .2710 .3000 .5890	.3530 .2300 .4860 .4510	1.0240 .3450 .4530 .2190	.7420 .4100 .1240 .3710	.3200 .4740 .6140 .5680	.4970 .7650 .7040 .4860	.6990 1.0620 .3800 .8450	.1560 .4220 .5120 .5760	.8960 2.3550 .8190 .7250
1,4960 3,0670 1,0650 2,2190 2,2750	.5220 1.4400 2.3060 1.8750 1.3050	2.5330 1.2350 .6530 .8950 3.8370	2.3060 .6960 .2570 1.2180 4.9720	2.0450 5.5190 4.3070 2.8800 4.7420	2.2710 1.1940 4.6760 3.1320 8.1780	2.0140 3.4150 .9910 1.8400 3.5840	.4910 5.0240 7.5690 4.2200 3.7980	7.3520 6.8730 3.6980 12.7720 3.2540
2.4850 1.2840 3.7790 2.7980 2.5600	5.5140 3.4650 4.2800 3.1600 5.4250	2.9630 4.9600 5.9260 3.9030 2.1560	3.0450 4.8500 4.7250 4.7730 1.9180	4.6500 1.9750 3.5390 6.3700 3.6460	5.3000 11.0740 4.5270 6.6660 3.3740	7.3910 7.7770 7.0400 11.7690 7.0000	8. 2260 5. 0200 4. 6090 6. 9790 9. 2830	9.7110 7.5720 10.4520 3.9480 15.9660
2.774 2.395 3.760 2.196 1.856	2.485 3.473 1.946 3.353 2.350	2.011 2.524 2.161 4.685 3.074	4.192 4.750 7.969 4.805 2.485	3.892 2.086 2.545 2.086 3.258	4.850 1.336 2.695 2.745	3.608 2.535 6.360 2.984 5.858	12.445 5.514 3.244 5.629 6.188	1.198 4.142 7.086 2.131 1.886
690 693 716 717 751	770 778 793 803 812	815 826 830 864 867	942 948 956 969 970	983 995 1,030 1,064 1,095	1,106 1,135 1,150 1,170 1,170	1,195 1,247 1,260 1,413 1,414	1,462 1,470 1,500 1,505 1,545	1,610 1,690 1,770 1,824 1,828
Ramsey Buffalo Lac Qui Parle Day Ramsey	Marshall Big Stone Benson Ramsey Pope	Brookings Kandiyohi Marshall Murray Sully	Ramsey Lincoln Marshall McGook Edmunds	Marshall Brown Benson Hamlin Brown	Lake Grant Benson Kidder Benson	Minnehaha Kingsbury Lincoln Marshall Traverse	Traverse Davison Nelson Lake Hamlin	Benson Nelson Lake Lyon Day
ZWEZZ	OENZE	o z o z o	NEENN	× o × o o	OESSS	S S M S M	X N Z N Z	SSSE
Irvine	Buffalo South Big Stone Mallard Lac Aux Mortes	Stnat	Morrison Renton Thief East Vermilion	Mud	Herman	Wall	Mud	Broken Bone

Control Cont									
String S	opt.dens	11111	11111	11111	11111	11111	156	11111	11
State Caste Caste State Caste Cast	color	42 16 25 21 27	8 £ 1 4	20 23 21 35	41 20 18 45 34	25 49 40 68	1 35 8 1	53 41 29 55 45	90
No. of the control Con	Н	7.60 7.92 7.86 7.98 7.98	7.27 7.40 8.20 7.80	7.53 7.56 8.60 7.55 8.13	7.48 8.73 6.40 7.40 8.80	8.60 8.70 8.27 8.38 8.90	9.60 7.77 8.90 7.91	8.00 8.80 7.98 8.51 9.40	8.20 8.04
No. of the control	ppm-B	.270 .580 .620 .580	.370 .270 .280 .290	.490 1.342 1.700 .430	.330 1.433 2.330 2.200	4.500 3.100 1.900 2.700 6.200	5.900 3.370 5.200 2.800	2.840 7.700 15.000 5.910 21.000	14.000 12.840
S SATING COUNTY N.	ppm-Mn	<pre><0 .780 .040 .490 .440</pre>	.010 .010 0000	1. 204 <0 1. 930	3.910	<0 .050 .140	1.100	.080 .00 3.090 .060	
State County Fymios cpm-6a cpm-8a cpm-8a cpm-8a cpm-8a cpm-8a cpm-6a cpm-7a cpm-7a	ppm-Fe	.060 .060 .110 .050	.050	.040	.010	.020	.060	.100 .120 .140 .050	- 080
Starte Gounty Frymitos epur-64 epur-74	ppm-Si02	14.000 20.270 20.980 3.650 27.010	34.330 10.850 12.000 7.500 9.500	14.130 22.365 23.000 32.750 12.870	20.080 12.333 5.530 15.000	16.000 6.100 7.870 8.400 7.900	6.700 4.470 4.300 16.060	15.120 1.200 15.880 7.090	3.200
Starte Gounty Frymitos epur-64 epur-74	tot-cat	19. 5640 20. 4400 20. 7860 23. 2990 24. 6620	29.0960 26.6350 25.9340 28.7930 28.3210	36. 6360 30. 8790 31. 8300 48. 9110 52. 1080	61.1040 61.7550 113.5800 105.5500 106.7000	115.5400 136.3000 146.1700 235.3500 172.1600	180,9500 264,0400 206,3100 228,3600 271,3000	291.5400 510.6900 1,160.2000 812.7800 952.8700	1,189,4000
State County Klymbos epm—76 epm—78 epm—78 epm—78 epm—78 epm—78 epm—79 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1,	e pm-F	.200 .280 .440 .350	.370 .250 .400 .600	.470 .515 .500 1.350	1.650 .233 .200 .200	.200 .100 .260 .230	.200		
Starte County K-publos epu—Ca epu—Ma epu—Na epu—Na epu—Ta epu—Sa Sulla S	e pm-T-N	.0230 .0180 .0240 .0320	.0890 .0210 .0350 .0310	.0480 .0490 .0060 .0210	.0180 .0230 .0790 .1010	.0240 .0020 .0310 .0770	.0240	.0770 .0100 .0180 .0840	.0480
State County K-jumbos epa—Ca epa—Hg epa—Ha epa—Ha hallon light of the county light l	e pm-C1	2.3410 2.2170 3.8270 3.0460 .7220	.3860 2.7070 2.7640 2.0870 3.0460	.6120 4.1300 6.8530 5.0840 1.8330	14.3820 7.6050 4.6810 17.4560 23.9420	20.8960 40.3260 30.2560 12.7970 15.9050	2.3970 8.9960 28.4820 58.9800 50.4000	59, 2680 62, 3220 22, 8980 136, 2900 36, 3780	215.7300
State County K-jumbos epa—Ca epa—Hg epa—Ha epa—Ha hallon light of the county light l	e pm-504	12. 7920 10. 9720 8. 8630 16. 6050 18. 9220	24.8210 17.0350 14.3100 19.7600 18.2210	30.7840 21.1970 2.5790 39.8840 38.8960	38.7400 42.5010 97.7600 82.7840 58.0320	62.4000 81.1200 103.0300 200.6100 126.8800	77.5840 246.6800 141.2300 167.8400 208.8000	217.1400 449.2800 1,087.8000 648.5200 534.5600	936,0000
State County Kymhos epa—Ca epa—Mg epa—Mg State County I,886 3,124 4,2210 11,7880 2.15 4,2210 11,7880 2.15 4,2210 11,7880 2.15 4,2210 11,7880 2.15 4,2210 11,7880 2.15 4,2210 11,7880 2.15 4,2210 11,7890 2.25 Monte floame 1,950 6.078 9,2230 11,7300 11,7300 2.25 Monte floame 2,325 7,700 16,1310 4,2330 2.25 Monte floame 2,325 7,700 16,1370 11,1360 2.25 Monte floame 2,360 7,700 16,1370 16,1370 2.25 Monte floame 2,360 7,700 17,1370 2.25 Monte floame 2,360 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,700 7,70	epm-alk	4.674 7.304 8.254 3.381 4.128	2.957 6.478 9.364 6.773 7.216	4.259 5.676 22.493 2.640 10.621	6.171 12.420 8.618 9.053 27.768	30.679 11.316 13.743 15.150 29.094	99.130 5.178 32.638 6.953 4.680		
State County Kymhos epm—Ca epm—Mg epm—R State County Kymhos epm—Ca epm—Mg Sully 1,886 3.144 4.3210 111	e pm-K	.5120 1.1780 .7550 .4680 1.0340	1.0320 1.7540 .9220 .9220 1.4340	1.7330 1.0570 1.9200 2.0990 3.2440	2.6570 6.5200 5.3680 3.9680 4.4030	3.2770 6.7580 6.2820 8.3200 9.9070	2.0220 9.6590 8.4990 6.5200 3.8100	11, 2050 6, 0420 20, 5640 28, 0500 7, 1680	44.5440
State County K-jumhos epu—Ca Sully 1,866 3.144 Sully 1,966 3.144 Shrower Homme 1,886 3.144 Shrower Homme 1,886 3.144 Shrower Homme 2,306 2.136 Marshall 1,974 5.205 Marshall 2,725 7.700 Benson 2,400 7.435 Marshall 2,723 2.470 Marshall 2,723 2.470 Marshall 2,723 2.470 Marshall 2,723 2.365 Marshall 2,723 2.365 Marshall 3,740 2.345 Marshall 3,740 2.345 Marshall 1,862 4.775 Marshall 1,862 6.423 Marshall 1,863 6.836 Marshall 1,974 6.836 Marshall 1,974 6.433 Marshall 1,974 6.433 Marshall 1,974 6.433 Marshall 1,970 6.439 Marshall 1,970 6.435 Marshal	e pm-Na				15.0730 29.9570 24.8250 58.7250 99.1800				848.2500 993.2400
State County K-jumbos N Nelson 1,866 Sully 1,936 Spink 1,936 Spin	epm~Mg	5.0200 4.3210 4.2060 9.4230 12.0240	16.1310 11.2750 8.7240 12.3450 12.2630	24.1960 8.2450 1.7280 10.3530 38.0230	18.7230 24.1960 78.1850 39.9160 2.4690	7.6540 46.6640 35.6770 152.1400 42.4670	.7490 154.6600 25.6780 63.3630 42.2000	68.6140 73.6590 856.9400 204.3100	292.1600 527.1800
S S S S S S S S S S S S S S S S S S S	e pm-Ca	3.244 3.144 2.136 6.078 5.205	7.700 2.470 1.846 7.435 2.096	3.877 4.775 .429 27.520 2.345	24.651 1.082 5.205 2.944 .649	.649 1.098 4.147 6.452	. 269 12. 475 . 309 8. 368 17. 840	3.248 3.393 20.509 3.283 1.397	4.491 14.002
S S S S S S S S S S S S S S S S S S S	K-pmhos	1,860 1,886 1,936 1,950 1111 1,974	2,267 2,325 2,360 2,400 2,460	2,723 2,952 2,970 3,565 3,740	4,618 5,153 7,203 8,440 9,530	9,690 10,600 11,717 12,642 12,900	14,000 15,013 15,300 16,214 17,366	21,056 34,800 42,725 47,721 55,000	64,200
S S S S S S S S S S S S S S S S S S S	County	Nelson Sully Spink Bonne Homme Kingsbury & Ham	Brookings Benson McHenry Foster Benson	Marshall Beadle Benson Charles Míx Marshall	Brule McPherson Day Benson Benson	Benson Stutsman Ramsey Day Kidder	McLean Day Kidder Nelson Lac Qui Parle	Ramsey Benson Codington Ramsey Lakota	Stutsman Nelson
Jake Name Rose	State		SZZZZ	8 8 8 8 8	SSSS	ZZZGZ	ZWZZE	ZZWZZ	ZZ
	Lake Name	Rose	East Oakwood Long Buffalo Lodge Juanita Twin	Fort Sisseton Byron	Red	Free People Tweady Devil's Bitter Stony	Ordway	Devil's (Mission Ray) Stink Medicine East Devils Cranberry	Stink